DISSOCIATION, FRAGMENTATION AND FISSION OF SIMPLE METAL CLUSTERS*

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I. INTRODUCTION

Dissociation, fragmentation, and fissioning processes underly physical and chemical phenomena in a variety of finite-size systems, characterized by a wide spectrum of energy scales, nature of interactions, and characteristic spatial and temporal scales. These include nuclear fission [1,2], unimolecular decay and reactions in atoms and molecules [3], and more recently dissociation and fragmentation processes in atomic and molecular clusters [4–6]. Investigations of the energetics, mechanisms, pathways, and dynamics of fragmentation processes provide ways and means for explorations of the structure, stability, excitations, and dynamics in the many-body finite systems mentioned above, as well as they allow for comprehensive tests of theoretical methodologies and conceptual developments, and have formed active areas of fruitful research endeavors in nuclear physics, and more recently in cluster science.

Under the general title of dissociation and fragmentation [7] processes in metal clusters, one usually distinguishes two classes of phenomena, i.e., (1) dissociation of neutral monomers and/or dimers, and (2) fission. The physical processes in the first class are most often referrred to as evaporation of monomers and/or dimers, since they are endothermic processes and are usually induced through laser heating of the cluster. The unimolecular equations associated with these processes are

$$M_N^+ \longrightarrow M_{N-1}^+ + M \ , \tag{1}$$

for monomer separation, and

$$M_N^+ \longrightarrow M_{N-2}^+ + M_2 \ , \tag{2}$$

for dimer separation (N denotes the number of atoms in the clusters [8]). The parent clusters M_N^+ have been taken here as being singly ionized, in order to conform with available experimental measurements [4]. Fission on the other hand, is most often an exothermic process and is due to the Coulombic forces associated with excess charges on the cluster. It

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has been found that the minimum excess charge required to induce fission is 2 elementary units (either positive or negative). In this case the doubly-charged parent cluster splits into two singly charged fragments, and the corresponding unimolecular equation can be written as

$$M_N^{2\pm} \longrightarrow M_P^{1\pm} + M_{N-P}^{1\pm}, \quad P = 1, ..., [N/2] \ . \tag{3}$$

It needs to be emphasized that fragmentation through fission involves most often the overcoming of a fission barrier, while momomer and dimer separation are barrierless processes [4].

A. Metal cluster fission and nuclear fission: Similarities and differences

Multiply charged metallic clusters (M_N^{Z+}) are observable in mass spectra if they exceed a critical size of stability N_c^{Z+} (e.g. for $Z = 2$, $N_c^{2+} = 27$ for Na and $N_c^{2+} = 20$ for K [4,9]). For clusters with $N > N_c^{Z+}$, evaporation of neutral species is the preferred dissociation channel, while, below the critical size, fission into two charged fragments dominates (for $Z = 2$, two singly charged fragments emerge). Nevertheless, at low enough temperature, such M_N^{Z+} ($N < N_c^{Z+}$) clusters can be metastable above a certain size N_b^{Z+}, because of the existence of a fission barrier E_b (for Na_N^{2+} and K_N^{2+}, $N_b^{2+} = 7$ [10,11]).

These observations indicate that fission of metal clusters occurs when the repulsive Coulomb forces due to the accumulation of the excess charges overcome the electronic binding (cohesion) of the cluster. This reminds us immediately of the well-studied nuclear fission phenomenon and the celebrated Liquid Drop Model (LDM) according to which the binding nuclear forces are expressed as a sum of volume and surface terms, and the balance between the Coulomb repulsion and the increase in surface area upon volume conserving deformations allows for an estimate of the stability and fissility of the nucleus [12,13].

We note that for doubly charged metal clusters with $N \leq 12$ microscopic descriptions of energetics and dynamics of fission, based on first-principles electronic-structure calculations in conjunction with molecular dynamics (MD) simulations, have been performed [10,11] (see section III.C.1 for details). Several of the trends exhibited by the microscopic calculations (such as influence of magic numbers, associated with electronic shell closing, on fission energetics and barrier heights; predominance of an asymmetric fission channel; double-humped fission-barrier shapes; shapes of deforming clusters along the fission trajectory portraying two fragments connected through a stretching neck) suggest that appropriate adaptation of methodologies developed originally in the context of nuclear fission may provide a useful conceptual and calculational framework for studies of systematics and patterns of fission processes in metallic clusters.

In this context, it is useful to comment on the earliest treatments of pertinent nuclear processes, i.e., fission [12,1] and alpha radioactivity [14,15,2]. Adaptation of the simple one-center LDM to charged metallic clusters [5], involving calculation of the Coulomb repulsive energy due to an excess charge localized at the surface, yields a reduced LDM fissility parameter $\xi = (Z^2/N)/(Z^2/N)_{cr}$, where $(Z^2/N)_{cr} = 16\pi r_s^3\sigma/e^2$ with the surface energy per unit area denoted by σ and r_s being the Wigner-Seitz radius (using bulk r_s and σ values, $(Z^2/N)_{cr} = 0.44$ and 0.39 for K_N^{Z+} and Na_N^{Z+}, respectively). Accordingly, a cluster

is unstable for $\xi > 1$ (implying that for K_N^{2+} with $N \leq 9$ and Na_N^{2+} with $N \leq 10$ barrierless fission should occur) with the most favorable channel being the symmetric one (i.e., when the two fragments have equal masses, which is only approximately true for nuclear fission, and certainly not the case for small metal clusters). For $0.351 < \xi < 1$, the system is metastable (i.e., may fission in a process involving a barrier), and for $0 < \xi < 0.351$ the system is stable.

At the other limit, α-radioactivity, which may be viewed as an extreme case of (superasymmetric) fission, is commonly described as a process where the fragments are formed (or as often said, preformed) before the system reaches the top of the barrier (saddle point), and as a result the barrier is mainly Coulombic [2]. We note here that asymmetric emission of heavier nuclei is also known (e.g., $^{223}Ra \rightarrow ^{14}C + ^{209}Pb$, referred to as exotic or cluster radioactivity [16–18]), and the barriers in these cases resemble the one-humped barrier of alpha radioactivity and do not exhibit modulations due to shell effects [18]. We also remark that such α-radioactivity-type (essentially Coulombic) barriers have been proposed recently [19] for describing the overall shape of the fission barriers in the case of metal clusters.

Although, several aspects of the simple LDM (e.g., competition between Coulomb and surface terms) and the α-particle, Coulombic model (e.g., asymmetric channels and a scission configuration close to the location of the saddle of the multi-dimensional potential-energy surface) are present in the fission of metal clusters, neither model is adequate in light of the characteristic behavior revealed from the microscopic calculations and experiments. Rather, we find that proper treatments of fission in these systems require consideration of shell effects (for a recent experimental study that demonstrates the importance of shell effects in metal-cluster fission, see Ref. [9b]). While such effects are known to have important consequences in nuclear fission (transforming the one-humped LDM barrier for symmetric fission into a two-humped barrier [20,2]), their role in the case of metal clusters goes even further. Indeed, as illustrated below (see section III.C.2) for the case of the magic Na_{10}^{2+} (8 delocalized electrons), shell effects can be the largest contribution to the fission barrier, in particular in instances when the LDM component exhibits no barrier (in this case the LDM fissility $\xi > 1$). In this respect, Na_{10}^{2+} is analogous to the case of superheavy nuclei, which are believed [21] to be stabilized by the shell structure of a major shell closure at $Z_p = 114$, $N_n = 184$ (Z_p is the number of protons and N_n is the number of neutrons; unfortunately such nuclei have not been yet observed or synthesized artificially).

B. Other decay modes in atomic and molecular clusters

In this chapter, we will concentrate on the unimolecular processes in metal clusters described by Eqs. (1−3). However, there is a variety of additional dissociation and fragmentation modes in atomic and molecular clusters (see reviews in Ref. [22]), which have been discovered experimentally or anticipated theoretically; among them we mention:

1. Unimolecular fission of triply and higher charged cationic simple metal clusters [6,23,24];

2. Metastability against electron autodetachment of multiply charged *anionic* atomic clusters [25–27] and fullerenes [26–28];

3. Fragmentation of cationic fullerenes via sequential evaporation of carbon dimers [29];

4. Ultrarapid fragmentation of rare-gas clusters following excitation (involving excimer formation [30]) or ionization [22];

5. Multifragmentation phase transitions according to microcanonical thermodynamics of highly excited atomic clusters [31]; and

6. Pathways and dynamics of dissociation and fragmentation of ionized Van-der-Waals and hydrogen-bonded molecular clusters [22,32].

C. Organization of the chapter

In the following, we will present jellium-related theoretical approaches [specifically the Shell Correction Method (SCM) and variants thereof] appropriate for describing shell effects, energetics and decay pathways of metal-cluster fragmentation processes (both the monomer/dimer dissociation and fission), which were inspired by the many similarities with the physics of shell effects in atomic nuclei (section II). In section III, we will compare the experimental trends with the resulting theoretical SCM interpretations, and in addition we will discuss theoretical results from first-principles MD simulations (section III.C.1). Section IV will discuss some latest insights concerning the importance of electronic-entropy and finite-temperature effects. Finally, section V will provide a summary.

II. THEORY OF SHAPE DEFORMATIONS

In early applications of the jellium model, the shape of metal clusters was assumed in all instances to be spherical [33,34], but soon it became apparent that the spherical symmetry was too restrictive [35,36]. Indeed clusters with open electronic shells (between the magic numbers N_e = 2, 8, 20, 40, 58, 92, etc...) are subjected to Jahn-Teller distortions [37]. By now it has been well established that a quantitative description of the underlying shell effects and of fragmentation phenomena (as well as of other less complicated phenomena such as Ionization and Vertical Electron Detachment) requires a proper description of the deformed shapes of both parent and daughter clusters (of both precursor and final ionic or neutral product in the case of ionization and vertical electron detachment).

A most successful method for describing both deformation and shell effects in simple metal clusters (i.e., those that can be described by the jellium background model) is the SCM, originally developed in the field of nuclear physics [38,2]. In a series of recent publications [25,26,28,39–45], the SCM was further developed, adapted, and applied in the realm of finite-size, condensed-matter nanostructures (i.e., metal clusters [25,26,39–43], but also multiply charged fullerenes [28], ^{3}He clusters [44], and metallic nanowires and nanoconstrictions [45]). Additionally, Refs. [46–49] have used semiempirical versions (see below) of the SCM to study the shapes of neutral Na clusters [46,47] and aspects of metal-cluster fission [48,49].

The SCM derives its justification from the local-density-approximation (LDA) functional theory and has been developed as a two-level method.

At the microscopic level, referred to as the LDA-SCM, the method has been shown to be a non-selfconsistent approximation to the Kohn-Sham (KS) −LDA approach [50]. Apart from computational efficiency, an important physical insight provided by the LDA-SCM is that the total KS-LDA energy $E_{\rm total}(N)$ [or in another notation $E_{\rm KS}(N)$] of a finite system of interacting delocalized electrons (or more generally of other fermions, like nucleons or ^{3}He atoms) can be divided into two contributions, i.e.,

$$E_{\rm total}(N) = \widetilde{E}(N) + \Delta E_{\rm sh}(N) \ , \tag{4}$$

where $\widetilde{E}$ is the part that varies smoothly as a function of the system size (e.g., the number, N of atoms in a metal cluster), while $\Delta E_{\rm sh}(N)$ is an oscillatory term accounting for the shell effects; it arises from the discretization of the electronic states (quantum size effect). $\Delta E_{\rm sh}(N)$ is usually called a shell correction in the nuclear [38,1] and cluster [25,26] literature.

Starting from the fundamental microscopic separation in Eq. (4), various semiempirical implementations (referred to as SE-SCM, see section II.B) of such a division consist of different approximate choices and methods for evaluating the two terms contributing to this separation.

As an illustration of the physical content of Eq. (4) (which as well serves as a motivating example for the SCM), we show in Fig. 1 the size-evolutionary pattern of the Ionization Potentials (IPs) of Na_N clusters, which exhibits odd-even oscillations in the observed spectrum in addition to the major features (major IP drops) at the magic numbers. Theoretical calculations at three different levels are contrasted to the experimental observations, namely, a smooth description of the pattern [Inset (a)], and two levels of shell-corrected descriptions — one assuming spherical symmetry [Inset (b)], and the other allowing for triaxial shape deformations [Fig. 1, main frame]. The progressive improvement of the level of agreement between the experimental [51,52] and theoretical patterns is evident.

Below, we first outline the microscopic derivation of Eq. (4), and subsequently we proceed with a presentation of the SE-SCM.

A. Microscopic Foundation of Shell Correction Methods – The LDA-SCM

The LDA-SCM approach, which has been shown to yield results in excellent agreement with self-consistent KS-LDA calculations [25,26], is equivalent to a Harris functional [53] approximation ($E_{\rm Harris}[\rho^{\rm in}]$, see below) to the KS-LDA total energy [50] ($E_{\rm KS}[\rho_{\rm KS}]$), with the input density $\rho^{\rm in}$ obtained through a variational minimization of an extended Thomas-Fermi (ETF) energy functional, $E_{\rm ETF}[\rho]$.

The property of the non-selfconsistent Harris functional to yield total energies close to the KS-LDA ones is based on the following equality:

$$E_{\rm KS}[\rho_{\rm KS}] = E_{\rm Harris}[\rho^{\rm in}] + O(\delta\rho^2) \ , \tag{5}$$

where $\delta\rho = \rho_{\rm KS} - \rho^{\rm in}$. Namely, the KS-LDA energy is, to second-order in $\delta\rho$, equal to the Harris energy.

Several recent publications have proven [54–56] the validity of equation (5) in connection with the Harris functional, which is often used in electronic structure calculations of